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The Determination of
Phosphates in Natural Waters

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The Determination of Phosphates in Natural Waters

BY

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THESIS

FOR THE DEGREE OF

BACHELOR OF ARTS IN CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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May 27th 1904

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Perry Barker (Under Dr. A. T. Lincoln)
ENTITLED Determination of Phosphates in
Water Colorimetrically.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Arts in Chemistry.

H. S. Grindley

HEAD OF DEPARTMENT OF

93632



The amount of phosphates in drinking waters undoubtedly throws some light on the purity of such waters. The potability of waters is impaired by the presence of decaying organic matter and one of the numerous changes produced by such decay is the change of organic phosphorous compounds to phosphates. Phosphates may also be present as a result of waters charged with carbonic acid, percolating through rocks and minerals. Hence early investigators held that potable waters might contain considerable amounts of phosphates. However, unpolluted waters often contain notable quantities of chlorides and nitrates, which only condemn them in the presence of other contaminating ingredients.

Until recent years no accurate and rapid method for the determination of phosphates in water had been devised. A number of gravimetric and colorimetric methods have been tried with various degrees of success. Mehner & Harvey^I evaporated one liter of the water to dryness, took up the residue with a little nitric acid and precipitated the phosphate as the phospho-molybdate with ammonium molybdate solution. But by this method the amount was too small to weigh accurately, it required too much time and considerable loss of phosphate occurred during concentration. Phipson^{II} precipitated the phosphate from a large volume of water with alum and an excess of ammonium, making the final precipitation with ammonium molybdate. This is a long process and later experiments, with a more delicate method showed that the precipitation was incomplete. Lepierre^{III} was the first to use a colorimetric method to determine phosphates in natural waters. He evaporated one liter of water,

dehydrated the silica by repeated evaporation with nitric acid, ignited strongly and filtered. The phosphate in the filtrate was precipitated with ammonium molybdate as the phospho-molybdate which, in the acid solution, imparts a yellow color to it. This solution was compared with solutions containing known amounts of phosphates precipitated in the same manner. Jolles and Neurath^{IV} used potassium molybdate instead of ammonium molybdate as the precipitating reagent. Jolles^V used the above method but removed the silica by evaporating a liter of water to dryness and igniting at 130° C. Woodman and Cayvan^{VI} evaporated fifty cc of the water in a porcelain dish with three cc of nitric acid (sp. gr. 1.07) and then heated at 100° C. for two hours. The residue was then taken up with a little cold water, acidified with nitric acid, precipitated as the molybdate and compared with known standards. Woodman^{VII} used this method to make quite extensive investigations on drinking waters, while Veitch^{VIII} used it to determine phosphoric acid in soil extracts. Schreiner^{IX} devised a method by which the phosphates and silicates in solution were determined simultaneously. His method is based on the fact that the silico-molybdate gives different depths of color by varying the conditions of precipitation, while the color due to phospho-molybdates remains the same under all conditions. He found that the color of the silico-molybdate was twice as great, if the ammonium molybdate and nitric acid were added one hour apart, as that color produced by adding them simultaneously. It is evident that the difference in color is equal to one half the silica present, so twice the difference subtracted from the reading of the color when both reagents were added together leaves the a-

mount of color due to phosphates. This method was used chiefly to determine P_2O_5 and SiO_2 in soil extracts.

A part of the experimental work was done on the dehydration method of Woodman and Cayvan^{VI} until Schreiner's^{IX} method was published. Then this method was tried. As the amount of silica is much greater than the phosphates in waters while the reverse of this is true in soil extracts, the accuracy of Schreiner's method is diminished. The chief object of the experimental work on the last method was to adapt it to the determination of phosphates in water.

Experimental Part

Reagents

Ammonium Molybdate-- 50 grams of the pure neutral salt were dissolved in 1 liter of distilled water.

Nitric Acid-- (sp. gr. 1.07) Approximately one part of acid (sp. gr. 1.42) to five parts of water.

Standard Phosphate Solution-- About two grams of pure crystallized sodium phosphate ($Na_2HPO_4 \cdot 12 H_2O$) were dissolved in one liter of water. The strength of this solution was determined by two methods: (1) by precipitating the phosphoric acid as magnesium ammonium phosphate according to Talbot^X and (2) by precipitation as the phosphomolybdate as directed by Blair^{XI}.

Standard Silica Solutions-- At first only an alkaline silica solution was used. This was made by dissolving freshly precipitated gelatinous silica in a sodium hydrate solution made by the action of

metallic sodium on water. In testing the dehydration method the silica was furnished by diluting this solution. Later, when work on the difference method began, an acid solution, made by dissolving crystallized Na_2SiO_3 in water and neutralizing with nitric acid, was used. The silica in both solutions was determined gravimetrically.

Apparatus

At first ordinary long 50 cc Nessler tubes were used but the diameter of these was too small to read the color closely. Later, tubes 25 cm long by 25 mm in diameter of colorless glass were used. The bottoms of these tubes were not as finely polished as most Nessler tubes. These had a capacity of 100 cc and were graduated with 25 cc divisions while one tube used to hold the standard solution was graduated to 1 cc and was connected by a side neck and tubing to a leveling bulb.

The camera at first consisted of two plane mirrors fastened to a ring stand and tilted at an angle of 40° . The tubes were held in an upright position between the two mirrors, the light passing from the bottom through the solution whose color is read by looking in the upper one. This form of apparatus was found to let in too much light around the sides of the tubes, so a camera closed on all sides except the front was constructed. A slight opening about 4 x 8 inches was made at the back to admit light to the lower mirror. However, instead of having a mirror at the bottom of the camera white porcelain plates were substituted. These do not throw so much light up through the solutions and so allow the yellow color due to

phospho-molybdate to be more easily read. Further, the differences in light due to changes in the sky are eliminated by using porcelain plates instead of a mirror. A north light was used entirely and as far as possible determinations were made in clear weather.

Dehydration Method

As stated above this is the method of Woodman and Cayvan VII. Fifty cc of the water together with 3 cc of HNO_3 (sp. gr. 1.07) are evaporated to dryness in a three inch porcelain dish. The residue is heated for two hours in a water oven at 100° C. to dehydrated all silica. Now the residue is taken up with fifty cc of cold distilled water, added in several portions, and filtered into fifty cc Nessler tubes. Two cc of HNO_3 (sp. gr. 1.07) and four cc of ammonium molybdate solution are added and the tubes placed in the comparison camera. After twenty minutes they are compared with tubes which contain known amounts of P_2O_5 and color reagents and have stood the same length of time.

The first tests made were to vary the conditions of the previous investigator's method. The authors had found that no temperature below 130° for less than one hour or 100° for less than two hours would bring about complete dehydration. In order to shorten the time required for the dehydration the residue was dried at 100° for five minutes, then ignited at a red heat for two minutes. The results are given in Table I.

Table I.

<u>P₂O₅ added</u>	<u>P₂O₅ found</u>	<u>% loss</u>
0.01	0.01	00
0.02	0.015	25
0.05	0.035	30
0.1	0.04	60
0.2	1.1	45
0.5	2.4	52

It is evident from these data that endeavoring to dehydrate the silica by ignition is out of the question.

Next the amount of dilute nitric acid added to precipitate the phospho-molybdate, was varied. The results of experiment are given in Table II.

Table II.

<u>HNO₃</u>	<u>Molybdate</u>	<u>Na₂HPo₄</u>	<u>HNO₃</u>	<u>Molybdate</u>	<u>Na₂HPo₄</u>
cc	cc	mg			
1	4	0.1	2	4	0.08
2	4	0.1	2	4	0.1
3	4	0.1	2	4	0.09
4	4	0.1	2	4	0.09
5	4	0.1	2	4	0.11
6	4	0.1	2	4	0.09
7	4	0.1	2	4	0.08
8	4	0.1	2	4	0.08
9	4	0.1	2	4	0.08
10	4	0.1	2	4	0.08

It is evident from this table that the amount of acid giving the greatest color is 5 cc. This amount was used afterward in all experiments and was later found to be the same amount used by Schreiner in his investigations.

The standards were found to develop their full color in about five minutes and never begin to fade within two or three hours. As a single standard was used in later experiments it was decided to let all determinations stand somewhat longer as this standard solution contained a large amount of phosphate. Twenty minutes was the length of time the tubes stood after the reagents were added before the color was read. Before any farther work could be done on this method the results of Schreiner's investigations appeared.

Difference Method

As previously stated this is the method of Schreiner^{IX}. One hundred cc of the water are placed in a flat bottomed tube and 5 cc of HNO_3 (sp. gr. 1.07) and 4 cc of ammonium molybdate were added. At the end of twenty minutes this is compared with a standard prepared in the same manner. This reading may be called the "a" reading. To another 100 cc sample 4 cc of ammonium molybdate are added. At the end of one hour 5 cc of HNO_3 (sp. gr. 1.07) are added and then in twenty minutes this sample is compared with a standard which was prepared as in the first reading. This may be called the "b" reading. Since the difference in these two readings represents one half the silica present, twice this difference subtracted from the "a" reading gives the color due to phosphates. The reagents used for this method are the same as those used in the dehydration method

except that an acid silica solution was also used. This solution was made by dissolving crystallized Na_2SiO_3 in water and neutralizing with nitric acid. The sodium phosphate solution used for these experiments was standardized by precipitating as ammonium magnesium phosphate, and ^{then} by the phospho-molybdate precipitation. The value of both silica solutions was determined by volatilizing with hydrofluoric acid. The values are for one cc.

Standardization of Sodium Phosphate Solution

	<u>1</u>	<u>2</u>
MgNH_4PO_4	0.00124	0.00122
Phospho-molybdate	0.00110	0.00111

Standardization of Silicate Solutions

	<u>1</u>	<u>2</u>
Alkaline solution	0.00164	0.00162
Acid solution	0.00252	0.00251

These solutions were diluted so that 1 cc equalled 0.1 mg. of SiO_2 or P_2O_5 .

The first set of experiments were run to check up Schreiner's factor for the difference in color depths. Known amounts of SiO_2 and P_2O_5 were diluted to 75 cc and compared as stated in the method. The dilutions were made to 75 cc instead of 100 cc because the tubes used held only 100 cc and would overflow when the precipitating reagent was added. The standard used contained 0.01 mg. of P_2O_5 per cc.

<u>SiO₂</u> added mg.	<u>Readings</u>	<u>"a"</u>	<u>"b"</u>	<u>Relation between</u> <u>two readings</u>
0.3	41	20		2.05
0.4	82	40		2.10 .05
0.6	122	61		2.00
0.8	162	82		1.93
1.0	198	98		2.02

It is evident from these that for all practical purposes the relation may be considered as one half. Since this is true the reading for SiO₂ with a P₂O₅ standard is equal to twice the actual value in SiO₂.

As the phosphates in water is low in comparison with the silica, considerable error in reading will occur. To remedy this a known amount of phosphate may be added in order to bring the amounts of the two ingredients nearly equal. To ascertain the amount of silica in several types of waters of this state the high and low silica content were tabulated in the following table from the analyses of the Illinois State Water Survey. The results are stated in parts per million.

Maximum and Minimum Amounts of SiO₂ in Illinois Waters

	<u>River</u>	<u>Spring</u>	<u>Deep Well</u>	<u>Shallow Well</u>
Maximum	11.3	65.6	64.2	51.8
Minimum	5.0	2.3	1.8	4.0

As the average amount of P₂O₅ in waters is between 0.5 and 5 parts per million, it is evident from the above values that the silica is present in large excess. Schreiner showed that his

method is applicable when the P_2O_5 and SiO_2 are about equal or when the P_2O_5 is present in excess. But it is desired to make the method applicable when the SiO_2 is in large excess. In order to determine P_2O_5 in water a series of solutions were prepared containing large amounts of SiO_2 and small amounts of P_2O_5 . But these small quantities of P_2O_5 could not be accurately determined and it was necessary to make the content of SiO_2 and P_2O_5 nearly equal. It was found by adding 0.5 mg. of P_2O_5 to each 75 cc of these solutions that as low as 0.05 mg. can be accurately determined. Therefore, we may conclude from the following table that adding this known amount of P_2O_5 to each 75 cc of water in order to make the SiO_2 and P_2O_5 approximately equal, we can determine them with a fair degree of accuracy. The lowest amount of P_2O_5 that can be accurately determined is 0.05 mg. per 75 cc or 0.65 parts per million.

Adding a Known Amount of P_2O_5 to Solutions of SiO_2 and P_2O_5

Content of Solution		Readings for 75 cc		Readings for Added			Found	
P_2O_5 mg.	SiO_2 mg.	a	b	P_2O_5	P_2O_5	SiO_2	P_2O_5 mg.	SiO_2 mg.
0.01	0.2	90	71	50	2	38	0.02	0.19
0.05	0.2	95	75	50	5	40	0.05	0.20
0.1	0.2	100	80	50	10	40	0.10	0.20
0.2	0.2	110	91	50	22	38	0.22	0.19
0.5	0.2	138	120	50	52	36	0.52	0.18
0.01	0.4	130	91	50	2	78	0.02	0.39
0.05	0.4	134	95	50	6	78	0.06	0.39
0.1	0.4	140	100	50	10	80	0.10	0.40
0.2	0.4	150	112	50	22	76	0.22	0.38
0.5	0.4	168	128	50	48	80	0.48	0.40

The same method of adding 0.5 mg. of P_2O_5 to each determination was used on some samples of water. The waters tested were divided into two classes: waters which may be considered unpolluted and waters plainly polluted. The results of the sanitary analysis and P_2O_5 determinations are given in the following tables and expressed in parts per million.

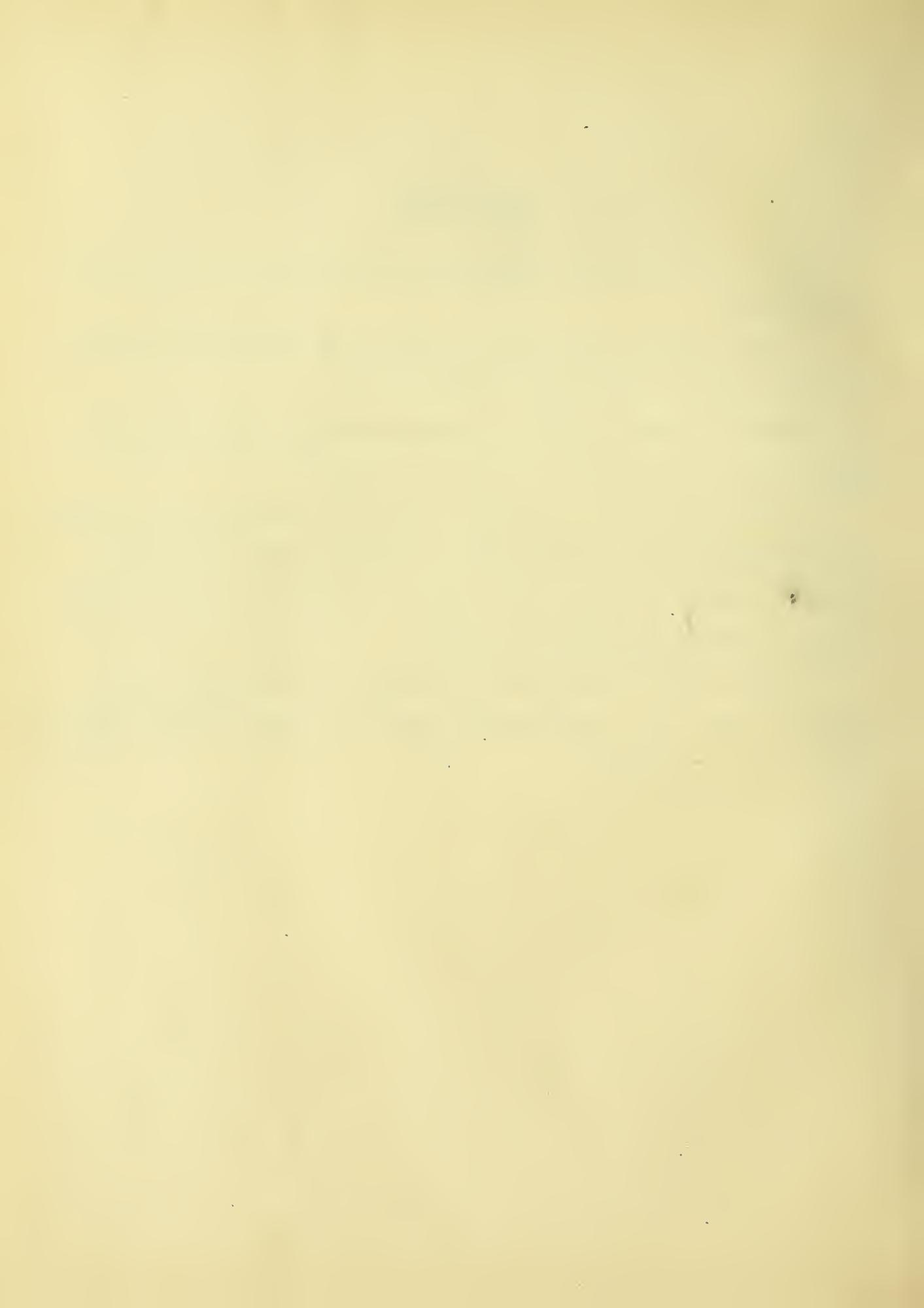
Unpolluted Waters

Polluted waters

Conclusions

From the experimental work herein presented we are justified in concluding:

- (1) That owing to the loss of phosphorous compounds the SiO_2 in waters cannot be obtained by dehydration;
- (2) That in the colorimetric determination of phosphates the deepest color is produced by adding 5 cc acid;
- (3) That the work of Schreiner has been confirmed and extended to the determination of phosphates in drinking water by adding a definite quantity of P_2O_5 to the water in order to make the content of P_2O_5 and SiO_2 approximately equal;
- (4) And that the method is applicable to the several types of water, - deep well, shallow well, river and spring waters found in the state of Illinois.



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